

Novel Pressure Induced Structural Phase Transition in AgSbTe₂

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We report a novel high pressure structural sequence for the functionally graded thermoelectric, narrow band gap semiconductor AgSbTe₂, using angle dispersive x-ray diffraction in a diamond anvil cell with synchrotron radiation at room temperature. The compound undergoes a B1 to B2 transition; the transition proceeds through an intermediate amorphous phase found between 17-26 GPa that is quenchable down to ambient conditions. The pressure induced structural transition observed in this compound is the first of its type reported in this ternary cubic family, and it is new for the B1-B2 transition pathway reported to date. Density Functional Theory (DFT) calculations performed for the B1 and B2 phases are in good agreement with the experimental results.

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Ternary semiconductors with a general formula ABX₂ (A = Cu, Ag; B = In, Ga, Sb; X = S, Se, Te) with chalcopyrite or rock salt structure are widely used for important technical and device applications. These compounds are found to be excellent candidates for the fabrication of optical frequency converters in solid state laser systems, photovoltaic devices and development of solar cells.^{1,2,3} While the Cu based chalcopyrites are mainly studied in connection with their photovoltaic applications, the Ag compounds find importance in thermoelectric, optical phase change and frequency conversion applications.^{4,5} Cubic AgSbTe₂ compounds with Pb doping have been recently shown to be excellent thermoelectric materials with high figures of merit, and are considered promising candidates for future energy production from heat sources.⁶ AgSbTe₂ with In and V doping undergo rapid crystalline - amorphous phase transitions on local melting; a property that is used widely to write and rewrite Compact Disks (CD) and Digital Versatile Disks (DVD).^{7,8} In comparison with the classical GeSbTe phase change memory alloy, AgVInSbTe is reported to have better erasability and cyclability in memory switching.^{7,8,9,10} The phase changes in these materials are temperature driven, and the previous studies focus mainly on doped thin films of AgSbTe₂. To our knowledge, no detailed structural reports are available for the host compound AgSbTe₂, under different temperature or pressure conditions.

AgSbTe₂ is isostructural to the rocksalt type II-VI chalcogenides. As the rock salt structure of most of the II-VI compounds is sensitive to pressure, changing from B1 to B2,^{11,12} one may expect AgSbTe₂ to display a similar crystallographic transition under pressure. The aim of the present study is to investigate AgSbTe₂ under pressure to explore the structural similarities with its binary analogues. In this paper, we present experimental evidence, for the first time, of a pressure induced structural transition from B1 (crystalline) to B2 (crystalline) with an intermediate amorphous state. This is a new pathway for this structural sequence and is unique in the ABX₂

family. This finding may open up new directions in the search for similar compounds of scientific and technological importance. Also, it forces us to develop theoretical models that can explain the pressure induced amorphization.

AgSbTe₂ has been prepared by a conventional solid state reaction method. Stoichiometric amounts of starting material were melted in a Bridgman furnace at 873 K for 24 hours, then cooled to ambient conditions. The reacted mixture was checked with x-ray diffraction (XRD) and found to be single phase. In each high pressure run, a small piece of sample cut from a pellet along with a ruby chip was loaded with silicone oil in a stainless steel gasket having a 180 μ m hole between 500 μ m culet diameter diamonds in a diamond anvil cell. XRD experiments were performed using a rotating anode x-ray generator (Rigaku) operating with an Mo target for run 1, and synchrotron x-rays with beam size 20 \times 20 μ m at HPCAT, Sector 16 IDB at the Advanced Photon Source for runs 2 and 3. The XRD patterns were collected using a MAR imaging plate (300 \times 300 mm²) camera with 100 \times 100 μ m² pixel dimension for 10-20 s. The images were integrated using FIT2D programme,¹³ and structural refinements were carried out by Rietveld method with RIETICA (LHPM) software package.¹⁴ The pressure at the sample site has been estimated using the standard ruby fluorescence technique and the newly proposed ruby scale of Holzapfel.¹⁵

At ambient conditions, AgSbTe₂ crystallizes in the rocksalt structure (*Fm* $\bar{3}$ *m* symmetry); the metal atoms located at Na sites at (0, 0, 0) and the Te atoms occupy the Cl sites at (0.5, 0.5, 0.5). The diffraction peaks at ambient pressure can clearly be indexed to an fcc lattice with cell parameter $a = 6.0780(1)$ Å.¹⁶ Upon compression, the diffraction lines remain sharp and systematically shift with pressure as shown in Fig. 1. From the refinements, a decreases at a rate of 0.024 Å/GPa, while the the Ag/Sb-Te distance decreases at 0.0118 Å/GPa. The small variation of the Ag/Sb-Te distance relative to a indicates the rigid bonding of the metal-chalcogen atoms.

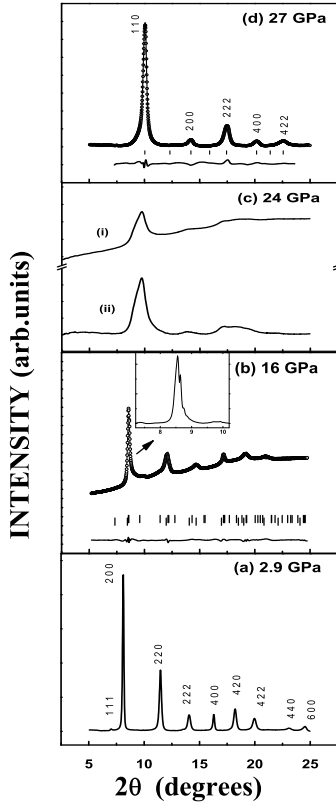


FIG. 1: Representative x-ray diffraction patterns with increasing pressure. The inset in (b) shows the splitting observed in the (200) line before amorphization. The Rietveld refinement for the $Cmcm$ phase is also shown. The refinement residual is $R_{wp} = 1.473$. Diffraction patterns at 24 GPa with back ground (i) and after back ground subtraction (ii) are shown in (c). The Rietveld plot for the x-ray diffraction pattern obtained at 27 GPa (d) shows the B2 structure.

The rocksalt phase is stable up to 15 GPa similar to the behavior of the isostructural compound $AgSbSe_2$ under pressure.¹⁷ At 16 GPa, we have noticed splitting of (200) and (420) peaks (inset of Fig. 1(b)) with broadening of other diffraction lines. These features clearly indicate the onset of a structural transformation. To our surprise, at 17 GPa, we observed a sudden drop in the intensity of all diffraction lines, leaving a halo peak located around $2\theta \sim 9.5^\circ$ with a significant broad background. The features observed in the XRD pattern at this pressure resembled the spectra typical for amorphous compounds. The amorphous phase persists up to 25 GPa as shown in Fig. 1(c).

The current models explaining the reconstructive phase changes of B1 structure are based upon either the Buehlers mechanism (i.e. the strain model) or the one emphasized by Watanabe *et al.* based on displacive transitions.^{18,19,20,21} Recently Toledano *et al.* studied different sequences for the pressure driven transitions from the B1 phase due to the coupling of the tensile

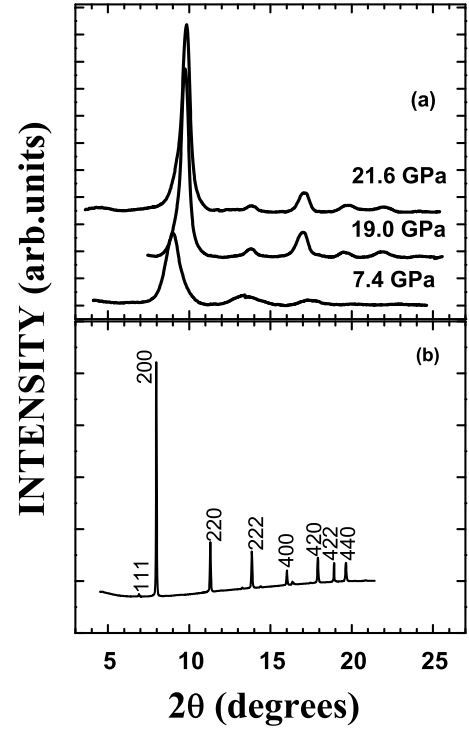


FIG. 2: (a) Sequence of x-ray diffraction patterns collected at different pressures while decompression. (b) Reappearance of diffraction lines corresponding to the B1 phase after heating the DAC for 100°C for 1 hr at ambient pressure.

and shear strains,²² and they suggest possible intermediate orthorhombic B33 ($Cmcm$) and B16 ($Pbnm$) structures. Previous high pressure structural studies on NaCl chalcogenides have shown transformation of NaCl phase to an intermediate orthorhombic phase ($Cmcm$ or $Pbnm$),^{23,24,25} we have examined the XRD pattern obtained at 16 GPa for similar types of distortions with $Cmcm$ and $Pbnm$ structures. Both $Pbnm$ and $Cmcm$ structures were considered during the Rietveld refinement, and a reliable fit has been obtained using the $Cmcm$ space group, with the Ag/Sb atoms located at 4a sites (0,0,0) and Te atoms occupying the 8d sites (0.75,0.25,0.5). The cell parameters obtained for the orthorhombic phase are $a = 3.7974(3)$ Å, $b = 4.238(4)$ Å and $c = 5.6358(1)$ Å. We find no considerable volume change between the B1 and orthorhombic phases as the two phases are found to coexist and the transition is continuous. Our results unambiguously show the distortions are related to the $Cmcm$ space group, and the features of $AgSbTe_2$ before amorphization indicate the distortions are similar to those observed in lead, calcium, and cadmium chalcogenides during the B1-B2 transition.^{23,24,25,26} These results closely agree with the earlier theoretical models explaining the rearrangement of atoms displaced between the layers during the B1-B2 transitions.

While comparing our results with similar compounds

exhibiting pressure induced amorphization, it is interesting to note that the corner linked tetrahedral α -quartz and isostructural compounds undergo transitions to a metastable polymorphic state before amorphization similar to AgSbTe_2 . In their molecular dynamics simulations based on enthalpy considerations, Chaplot and Sikka,²⁷ and later, Nandhini Garg and Surinder Sharma,²⁸ showed that above 12 GPa, the $Cmcm$ phase is favorable. The experimental observation of the disordered $Cmcm$ phase before amorphization in $\alpha\text{-FePO}_4$ by Pasternak *et al.*,²⁹ and in GaPO_4 by other groups, confirm this scenario.³⁰ In conjunction with the above, the orthorhombic $Cmcm$ phase is energetically favoured in AgSbTe_2 while approaching from B1 to a denser phase. Since simultaneous occurrence of crystalline and amorphous phases has been seen in FePO_4 , and also partial amorphization is reported in Co(OH)_2 by Nguyen *et al.*,³¹ we have examined the relative abundance of the crystalline phase if any, in the amorphous region. As seen in Fig. 1(c), there are no significant crystalline features identified, only a major halo peak. This fact eliminates the possibility of coexisting crystalline and amorphous phases. Interestingly, at 26 GPa, the diffraction lines started to reappear, showing the transformation of the amorphous state to a new crystalline phase. The observed x-ray diffraction pattern showed few peaks, and the refinement clearly indicated the existence of a CsCl phase with cell parameter $a = 3.4500(3)$ Å. The CsCl phase was found to be stable up to 30 GPa as shown in the Fig. 1(d).

The observation of $Cmcm$ orthorhombic distortions and an intermediate amorphous phase, while undergoing transition from the six fold coordinated B1 phase to eight fold coordinated B2 phase, clearly indicates a coordination frustration taking place in AgSbTe_2 due to the defect cubic structure and movement of Te atoms under pressure. This fact is consistent with the temperature driven amorphous state, observed in the doped family, where doping may increase internal defects, so that amorphization can be easily induced by temperature. Even though the structural transitions in AgSbTe_2 resemble SnI_4 ,³² the mechanism of amorphization is rather different. In the latter compound, molecular dissociation similar to BaAs is observed where a kinetically frustrated solid state amorphization is due to a change from fourfold to sixfold coordination.³³

Selected diffraction patterns during decompression are shown in the upper panel of Fig. 2. The crystalline peaks corresponding to the CsCl phase remained down to 12 GPa. Below 12 GPa, we observed broadening of the peaks, and transformation to amorphous state, showing hysteresis in the transition from CsCl phase to amorphous phase. The amorphous features remained even after releasing the pressure in the DAC, with a partial crystallization to B1 phase. The DAC was heated in an oven for 100°C for 1 hr, and diffraction patterns were taken. Surprisingly, sharp diffraction lines corresponding to B1 phase reappeared as shown in the bottom panel of Fig. 2, and the B1 phase is retained with a lattice constant

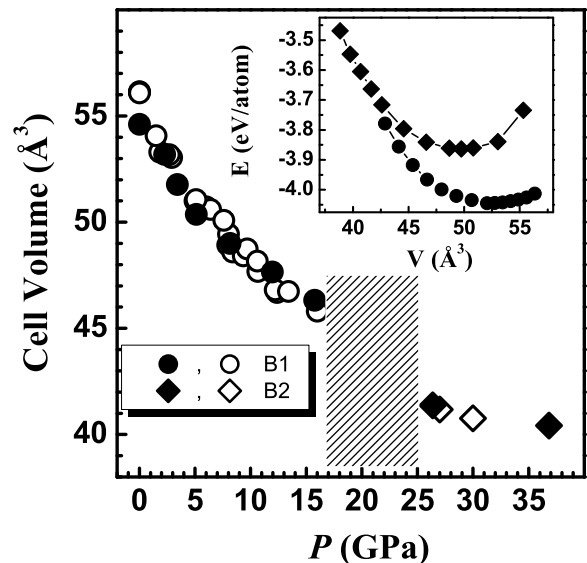


FIG. 3: $P - V$ data for AgSbTe_2 . The open symbols (circles denote B1 and diamonds B2) are the experimental data and the solid symbols represent the theoretical calculations for both phases. The amorphous phase is observed in the shaded region. (Inset) Binding energy curves for the B1 and B2 phases of AgSbTe_2 .

consistent with the initial ambient pressure value. These facts suggest that the pressure induced amorphous state in AgSbTe_2 is reversible, and thermal annealing supplies the energy to overcome the amorphous-crystalline energy barrier. This activates the recrystallization process back to the B1 phase identical to that observed in AlPO_4 and KH_2PO_4 (KDP).^{34,35}

In order to understand the stability of B1 and B2 phases observed experimentally, we have performed density functional theoretical (DFT) calculations using the FHI98MD code,^{36,37} local density approximation (LDA),³⁸ and norm conserving pseudo potentials. Troullier-Martins type pseudopotentials were generated for Ag, Sb, and Te atoms and extensive convergence tests were carried out in order to check the dependency of the number of k -points and plane waves.³⁹ The electronic wave-functions were expanded in plane-wave basis set with an energy cutoff of 71 Ry. Energy convergence was achieved with an accuracy of 10^{-4} eV. The k -point integration was performed with mesh points corresponding to 8 k -points in the Brillouin zone.

Binding energy curves show that the B1 phase is energetically favorable by 0.18 eV/atom relative to the B2 phase at ambient conditions as shown in Fig. 3. The calculated lattice constant of the B1 phase is 5.93 Å. This is in excellent agreement with the experimental value of 6.08 Å and compares favorably to other calculated values of 5.676 Å and 6.29 Å by M. Luo *et al.*⁴⁰ and R. Detemple *et al.*,⁵ respectively. Calculations performed for the B2 phase reveal that it is favoured around 26 GPa. More de-

tailed calculations to understand the intermediate phases are in progress.

A fit of the experimental $P - V$ data for the B1 phase, with the second order Birch-Murnaghan equation of state, yielded a bulk modulus of $B_0 = 45(2)$ GPa with $B'_0 = 4.8$. Even though the lattice constant is underestimated 2% compared to the experimental value, the bulk modulus 44.5 GPa, obtained theoretically, is in good agreement with the experimental value, when compared with the previous reports. For direct comparison of the equation of state, the theoretical volume is scaled to the experimental values as shown in Fig. 3.

In conclusion, we have demonstrated a new structural sequence in the functionally graded material AgSbTe_2 , which exhibits a B1 to B2 transition with an intermediate amorphous phase. The results of the ab initio simulations strongly support the pressure induced structural

transitions.

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